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THERMALLY STIMULATED DISCHARGE CURRENT ANALYSIS OF EPOXY RESINS--ETC(U)
APR 79 W A SU, T CHANG, S H CARR N00014-78-C-0276

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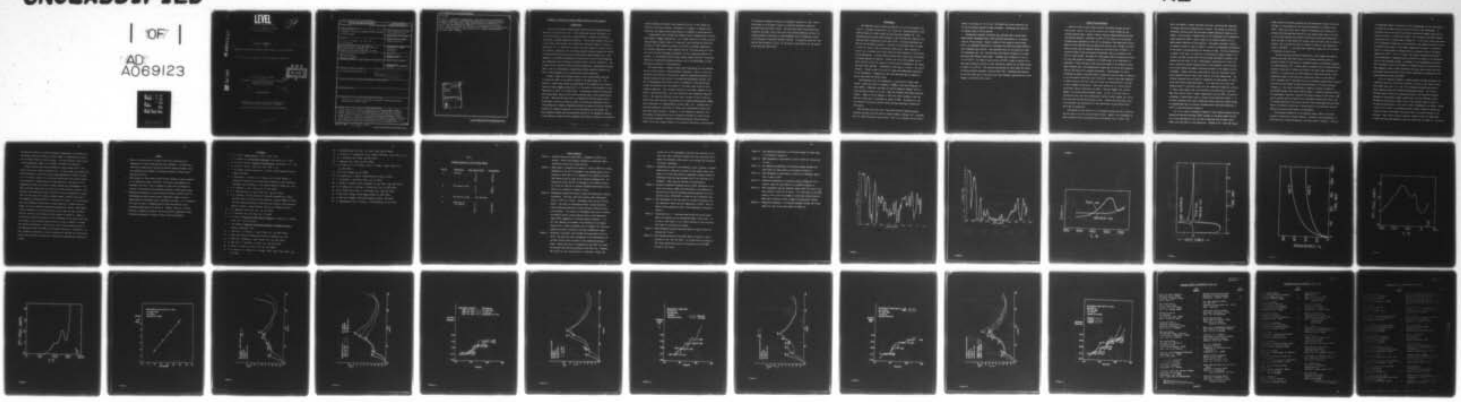

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TECHNICAL REPORT NO. 1

"THERMALLY STIMULATED DISCHARGE CURRENT ANALYSIS OF EPOXY RESINS"

by

W.-F. A. Su, T.-D. Chang, S. H. Carr, and J. O. Brittain

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The epoxy resin system, tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) cured with 4,4'-diaminodiphenylsulfone (DDS) has been studied. Primary emphasis has been placed on characterizing molecular relaxation processes as can be detected by Thermally Stimulated Discharge Current (TSDC) analysis. Ancillary characterization methods, including calorimetry, spectroscopy, and mechanical properties, have also been employed. It is seen that TSDC clearly reveals differences which can systematically be

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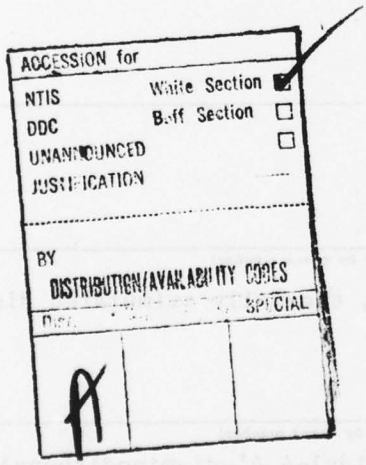
related to: composition (formulation), cure time, and cure temperature. At least 4 individual contributions to the molecular relaxation processes occurring in the temperature range 100-250°K have been identified, but not all such contributions are sensitive to the make-up of the resin itself. Research presented in this report gives evidence to the capabilities of our research seeking to make progress into a deeper understanding of such epoxy resin systems.



"THERMALLY STIMULATED DISCHARGE CURRENT ANALYSIS OF EPOXY RESINS"

INTRODUCTION

For over two decades, thermosetting resins based on polyepoxides have been put to practical use (1,2). Their advantages include reasonable cost for such attractive properties as high mechanical strength, high chemical resistance, and high temperature stability. A great many chemical variations on the epoxy resin systems can be achieved by different chemical structures being used (3). In virtually all cases, the resin system is created in which two different components, one containing epoxide functional groups and another containing base functional groups, are physically mixed together (4). Subsequently, a step-wise polymerization reaction will occur at rates depending upon temperature and continuing until some state of cure is reached (5). One or more of the reactants in most practical systems has a functionality greater than 2, and as a consequence, polymerization builds toward an infinite network of chain segments as the reaction goes toward completion.

Curing of these resin systems results in the reacting mass being able to retain the shape of the vessel in which it has been placed (5). The ability to retain shape either is established by the formation of an infinite network of chain segments (gelation) or is the result of vitrification at the temperature at which it is being cured. A conspicuous problem in conjunction with curing epoxy resins is the rather pronounced heat of the polymerization reaction. This heat may give rise to a temperature build-up within the reacting mass, so great care must be taken to prevent this exothermic effect from causing local chemical degradation within the material and from creating gradients in residual stress due to local differences in cure history (6). Such residual stresses may have measurable effects on the mechanical behavior of the material, either from the standpoint that they are additive to externally

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applied stresses and thereby cause premature failure, or they change the character of molecular mobility sufficient, for example, to depress microplasticity that might provide some measure of toughness to these materials.

Systems which have vitrified may undergo further polymerization reactions when heated to higher temperatures. It is common practice in curing practical epoxy systems to subject them to a "postcure", which involves an additional increment of time (usually an excess of an hour) at elevated temperatures. The possible existence of other chemical effects (7,8) associated with "postcure" have not been thoroughly documented, but two conspicuous effects are notable: 1) the specimen yellows almost always during "postcure", indicating additional, non-network building reactions, and 2) the development of high temperature stability in these materials.

The recent advent of superior epoxy resin formulations (9) has expanded the use of such resins in fiber-reinforced composites. This, in turn, has permitted the evolution of new kinds of composite engineering materials for advanced structural applications, including high-performance aircraft (10). The correspondingly more severe service requirements of such applications raises new questions about the behavior of the epoxy resin itself in such composite materials. This includes stability of the resin, adhesion of the resin to reinforcing fibers, and crack initiation and propagation characteristics. The research described in this report focuses on one of these advanced epoxy resin systems, tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy cured with 4,4'-diaminodiphenyl sulfone (DDS) (11). Although some of its usual mechanical properties are known, many uninvestigated effects may exist with these materials. Therefore, it was regarded as important that such aspects as mechanically active relaxation processes be characterized. A relatively new method, Thermally Stimulated Discharge Current analysis (TSDC) (12,31) was thought possibly to be unusually effective in investigation

of relaxation processes, because it is unusually sensitive to small effects and because it is extremely capable of resolving individual relaxation processes from each other (14,15). The particular merit of characterizing relaxation processes lies in the notion that certain mechanical effects, including yielding, fracturing, or work-hardening, may be intimately related to the existence of molecular mobility (16-19). It should be noted that this idea has been advanced, in part, on the basis of work done in our own laboratories using the TSDC method.

EXPERIMENTAL

The TGDDM/DDS system studied was supplied to us via the McDonnell Aircraft Co., McDonnell Douglas Corp., St. Louis, MO. Characterization of the chemical make-up of these resins has been reported elsewhere (9). The ingredients were already mixed together at the time they were received, and they have been continuously stored below $-44^{\circ}C$. Individual specimens are made by the following procedure. A portion of the uncured resin is heated to $120^{\circ}C$ for 10 min. under a mechanical pump vacuum. Next, material is poured onto a polished Teflon plate which had been preheated to the desired curing temperature. A second highly-polished Teflon plate (also pre-heated) is pressed against the material. Spacers are also placed between the two Teflon plates to serve as a means of controlling the thickness of the resulting epoxy resin specimen. Thicknesses in the range of .03 mm to 1 mm can be obtained. Curing is done in an oven for times and temperatures prescribed in the experiments. Subsequently, the cured specimens may be removed by gently separating the Teflon plates.

Investigations have also commenced on a second kind of epoxy resin system: diglycidyl ether of bisphenol A (DGEBA) cured with diethylene triamine (DETA). DGEBA was resin DER 332 from Dow Chemical Company, with an epoxy equivalent weight of 172-176. DETA was obtained from Fisher Scientific Company. DGEBA is vacuum degassed at $60^{\circ}C$ and, after cooling at room temperature, mixed with a stoichiometric amount of DETA. The mixture is cast onto sheets of polyvinyl chloride, which had been previously cleaned with isopropanol.

TSDC analyses were done with a Toyo-Seiki Electret Thermal Analyzer (obtained through the Atlas Electric Devices Company, Chicago, IL). Specimens used for these experiments were between 2 and 3 cm in diameter and had thick-

nesses in the range of .03 to 1 mm. Gold metal was vacuum evaporated onto the top and bottom surfaces of these specimens. Thermograms were obtained at heating rates of 2°C per minute.

Differential scanning calorimetry was performed with a Perkin Elmer Model DSC-IB; thermograms were either obtained isothermally or at heating rates of 1°C per minute. Tensile testing is done using an Instron Model TT-C-L, on specimens fabricated in accordance with ASTM test method D638-71a; type V geometry was utilized. Test specimens were cut from sheets of resin of thicknesses near 1 mm. Surfaces were very lightly abraided in the axial direction with 600-grit emery paper. Specimens were strained at a rate of 5×10^{-3} min^{-1}. For Resin A cured 4 hours at 150°C, stress at failure is in the range 13,000 psi, strain is 0.08, and elastic modulus for 1% offset strain is about 1.9×10^{5} psi. The infrared spectroscopy was done using the Fourier Transform Infrared Instrument, Nicolet Model 7199. Absorbance was measured as the area under each of the peaks with their baseline constructed as a chord tangent to the sides of the peak.

RESULTS AND DISCUSSIONS

Extent of cure in epoxy resin is often established through infrared spectroscopy (19,21), and such has proved to be a useful method for the research reported here. Figure 1 shows a typical infrared spectrum obtained from uncured material. Absorbance at 800 cm^{-1} was taken to be an internal thickness band; absorbance at 910 cm^{-1} is assigned to the epoxy group (22,23). Figure 2 is an infrared spectrum taken after partial cure. Changes in several peaks are seen, and the chemical results of cure can be seen in Table I. It is seen in Table I that the standard formulation, Resin A, achieves a cure level on order of 93%. An excess of curing agent, Resin B, permits the extent of cure, when judged by consumption of epoxide group, to go essentially to completion. Since one expects many chain ends simply to be capped by curing agent residues (24), the macromolecular network may not be any more extensive than for the case of the standard formulation. Interestingly, the resin containing an excess of epoxide (Resin F) appears to cure at least as completely as the standard formulation resin (Resin A). There is also some suggestion in Resin F spectra that the longer cure times are associated with a decrease in ester linkage concentration. These ester groups are in a second epoxide constituent, whose concentration is small. This may suggest that chemical damage is occurring during extended curing. In fact, it is seen from the spectroscopy data that the polymerization reaction itself changes very little with cure time carried beyond several hours. Further work along these lines is anticipated, but implications of this observation on post-curing treatments may be significant.

Calorimetry is also known to be an informative method for use in monitoring the state of cure of an epoxy resin (25,26). Figure 3 is a thermogram of Resin B which had been previously given an incomplete cure at 120°C. The

first run reveals a typical exothermic reaction, indicating the resumption of curing reactions as temperature is elevated. The second run shows that exothermic reactions over the previously scanned temperature range are now absent. One can detect a slight offset in the thermogram in the temperature range centered at 220°C. This is taken to be possible evidence for the glass-rubber transition of this material. Isothermal calorimetry results, an example of which is shown in Figure 4, provide an independent determination of the extent of polymerization as a function of time. One notes immediately in Figure 4 that there is difficulty in obtaining the initial stages of the reaction, as they coincide with the very strong instrumental transient that persists for the first 1.2 min. Nevertheless, subtraction of a first run from a second run permits identification of the exothermic reaction itself, as it occurs during the moments following placement of the sample into the instrument. Figure 5 has been constructed by using the isothermal calorimetric method on batch A epoxy resin cured at two lower temperatures. The fraction converted has been based on consumption of epoxy groups, as determined from infrared spectrophotometry. It is seen that both curves rise asymptotically to conversion levels that are themselves incomplete, and this is taken to mean simply that vitrification is occurring prior to gelation. When this resin is cured at higher temperatures, such as 180°C, the percent conversion of epoxy groups rises to values as were reported in Table I. It has been determined that these incompletely cured resins will indeed exhibit an exotherm when they are scanned calorimetrically from room temperature to 300°C, as was illustrated by Figure 3.

One of the primary experimental methods of this research program concerns Thermally Stimulated Discharge (TSDC) analysis of the epoxy resins (27,28). Part of the experimental work concerns an idealized kind of epoxy resin: DGEBA cured with DETA at room temperature. Figures 6 and 7 show TSDC thermo-

grams obtained from these materials over the temperature ranges from liquid nitrogen to room temperature and from room temperature to slightly above 200°C. These data reveal that a wealth of information will eventually be obtained from thorough TSDC analysis of such simple epoxy resins, but much of our initial research has actually focused on the Hercules formulations. Thus, the rest of this report will concern itself with that line of materials. Further, data presented here will be limited to TSDC over the temperature range of 100-300°K. It is within this temperature range that the so-called β relaxation process occurs.

Previous work has attributed relaxations in this temperature range to motions associated with small parts of the polymer molecules, such as motional freedom of side groups or crackshaft motions of methylene sequences in polymer backbone (29). Because there are dipolar parts of these molecules, dielectric detection of effects occurring at the repeat unit size-scale is possible. It appears that the TSDC analysis of these epoxy resins in this temperature range is also detecting a dielectric effect, as the electrostatic charging (30) of specimens results in discharge currents whose integral (the total stored charge) is directly proportional to initial polarizing voltage, E_p. The linear relationship in question is shown in Figure 8; polarizing voltages above about 30 KV/cm begin to evidence saturation effects. All experiments, therefore, involved polarizing voltages in this linear range, and we conclude that data shown in all subsequent figures arise from a kind of volume polarization effect which is most likely associated with some small amount of preferred orientation of dipolar parts of the molecules achieved during the initial poling stage of an experiment.

The standard formulation of the Hercules resins, Resin A, has been studied as functions of curing condition. Specimens cured incompletely at 140°C give rise to TSDC thermograms of the kind shown in Figure 9. There is

a considerable amount of structure in these thermograms, and the time effects of curing can be seen clearly to have its effect on the thermograms. Of particular note is the lack of any obvious correlation between peaks seen in material cured for 1.5 hours and 5 hours. Brief curing at different temperatures gives rise to effects seen in Figure 10. In this case, there does appear to be a systematic change that can be detected, even though the extent of cure is significantly larger for the higher temperatures involved. In addition, there is a larger amount of charge stored in specimens cured at the highest temperature, 181°C. It is, of course, the primary challenge in analyzing these thermograms of assigning specific molecular processes to the individual parts of the discharge process. An example of such assignments was made by Ochi and Shimbo (31,32), who proposed a crankshaft motion in flexible backbone segments, based on their observation that many epoxy resins, both with and without phenyl moities in their chains, exhibited β relaxations in this same temperature range (120-220°K).

It is not presently possible to define exactly how many individual contributions there are to this data "envelope", but use of the "partial heating" method (see refs. 14, 15 and 17) of discharge analysis does permit a first approach toward the complete understanding desired. The "partial heating" method involves the sequential heating of an initially polarized specimen to progressively higher temperatures, and the discharge current obtained in the earliest stages of each of the heating stages is taken to be directly proportional to the rate at which discharging is occurring. Making a plot of ln I, where I is discharge current, versus reciprocal temperature creates a linear relationship from whose slope an activation energy can be obtained. Then, plotting these activation energies versus the temperature at which the slope was measured yields the result seen in Figure 11, One notes

the general increase in activation energy as temperature is increased, but one further notes that there are certain ranges of temperature over which the activation energy is fairly constant. For the particular case of Resin A, such temperature ranges are 115-140°K, 165-185°K, and 185-215°K.

Similar analyses have been performed for epoxy resins B and E, and typical data can be found in Figures 12-17. In these cases, the formulations were cured more or less fully, using curing temperature of 181°C and times of 2 or 12 hours. Again, it is seen that TSDC analysis does reveal changes in the dielectric characteristics of these materials. One thing to note immediately is that the activation energy plateaus are approximately at the same activation energy value for each of the three resins in question. The plateau in the temperature range 120-150°K is fairly insensitive to formulation, but the upper two activation energy plateaus, especially the one in the temperature range 200-230°K is affected in more cases. It is anticipated that a more complete curing reaction simply means both a higher molecular weight and a more completely developed macromolecular network. When making a direct comparison of the three materials cured under the same condition, 181°C for 12 hours, one obtains the data observed in Figure 16. Again, it is seen that the general character of the thermogram is the same in each case, but looking at the activation energy spectra, as seen in Figure 17, reveals some distinct differences. Specifically, the activation energy plateau in the temperature range 150-180°K is particularly sensitive to formulation. We will, therefore, anticipate in future research that thie may be a particularly signal effect on which correlations of mechanical properties may successfully be made.

Summary

1. Extent of curing reaction in epoxy resins can be monitored via a combination of infrared spectroscopy and calorimetry. No significant additional polymerization reaction is detected during prolonged curing, but preliminary data suggest the possible existence of some chemical degradation effects.
2. TSDC analysis of cured epoxy resins has been studied, to date, primarily in the temperature range, 100-300°K. The broad β peak exhibits considerable "structure", and it promises to prove rich in information related to polarization and relaxation processes in these epoxy resins.
3. Temperature dependence of a mean activation energy calculated from the discharging processes reveals several temperature ranges in which a single molecular relaxation event is probably occurring. It is recognized (33) that the task of assigning specific molecular motions to such activation energy spectra is difficult. However, there is a rational approach to making the analysis, and the scientific significance seems sufficiently important to strive to have it done successfully.

REFERENCES

1. W. G. Potter, Epoxide Resins, Iliffe, London, 1970.
2. P. F. Bruins, ed., Epoxy Resin Technology, Interscience, N.Y., 1968.
3. H. Lee and K. Neville, Handbook of Epoxy Resins, McGraw-Hill, N.Y., 1967.
4. H. Lee and K. Neville, Insulation, Dec. 1960, p. 87.
5. J. K. Gillham, Technical Report No. 1, Office of Naval Research Contract N00014-76-C-0200.
6. S. Pasatcioglu, J. Hassler, A. L. Fricke, and H. McGee, "Effect of Temperature Gradients on Cure and Stress Gradients in Thick Thermoset Castings", paper delivered at 71st Annual Meeting of AIChE, Nov. 1978.
7. H. C. Anderson, J. Appl. Polym. Sci. VI, 484 (1962).
8. J. C. Paterson-Jones, J. Appl. Polym. Sci., 19, 391 (1975).
9. J. F. Carpenter, "Quality Control of Structural Nonmetallics", Annual Technical Report to Office of Naval Research, Contract N00019-76-C-0138, and "Test Program Evaluation of Hercules 3501-6 Resin", Final Technical Report to Office of Naval Research, Contract No. N00019-77-C-0155.
10. M. E. Waddoups, Polym. Eng. Sci., 15, 160 (1975).
11. J. A. McGroaty, Ind. Eng. Chem., 52, 17 (1960).
12. S. H. Carr, in Electrical Properties of Polymers, D. Seanor, ed., Academic Press, N.Y., 1979 (in press).
13. J. van Turnhout, Thermally Stimulated Discharge of Polymer Electrets, Elsevier, Amsterdam, 1975.
14. Y. Aoki and J. O. Brittain, J. Appl. Polym. Sci., 20, 2879 (1976).
15. Y. Aoki, PhD. Thesis, Northwestern University, Evanston, IL, 1977.
16. Y. Wada and T. Kasahara, J. Appl. Polym. Sci., 11, 1661 (1967).
17. Y. Aoki and J. O. Brittain, J. Polym. Sci., 15, 199 (1977).
18. N. Shito, J. Polym. Sci., Part C, No. 23, 569 (1968).
19. O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, Anal. Chem., 23, 277 (1951).

20. H. Dannenberg and W. R. Harp, Jr., Anal. Chem., 28, 86 (1956).

21. J. Feltzin, D. M. Longenecker, and I. Petker, SPE Trans., April 1965, p. 111.

22. W. A. Patterson, Anal. Chem., 26, 823 (1954).

23. J. Bomstein, Anal. Chem., 30, 544 (1958).

24. D. M. French, R. A. H. Strecker, and A. S. Tompa, J. Appl. Polym. Sci., 14, 599 (1970).

25. R. A. Fava, Polymer, 9, 137 (1968).

26. S. Sourour and M. R. Kamal, Thermochimica Acta, 14, 41 (1976).

27. J. B. Woodard, J. Electronic Matls., 6, 145 (1977).

28. T. Tanaka, S. Hayashi, and K. Shibayama, J. Appl. Phys., 48, 3478 (1977).

29. E. F. Cuddiny and J. Moacanin, J. Polym. Sci., A-2, 8, 1627 (1970).

30. P.K.C. Pillai and M. Goel, J. Electrochem. Soc., 120, 395 (1973).

31. M. Ochi and M. Shimbo, Nippon Kagaku Kaishe, 6, 1004 (1976).

32. M. Ochi and M. Shimbo, ACS Polymer Preprints, 20(1), 706 (1979).

33. J. Vanderschueren and A. Linkens, J. Electrostatics, 3, 155 (1977).

Table I

INFRARED ANALYSIS OF 3501-6 EPOXY RESINS

Our ID	Formulation	Cure time @ 181°C	% Conversion
A	Standard	0	0
		2	93
		8	94
		12	94
		20	93
B	10% excess in DDS	0	0
		2	92
		4	88
		8	100
E	20% deficit in DDS	(not analyzed)	
F	20% excess of one epoxide	0	0
		2	86
		4	90
		8	92
		12	93
		20	93

Figure Captions

Figure 1. Infrared spectrum of epoxy Resin A, degassed at 140°C for 10 minutes. This is the standard formulation of Hercules 3506-1 essentially without any curing reaction.

Figure 2. Epoxy Resin A, prepared as in Figure 1, cured at 158°C for 5 hours. Adsorbance at 910 cm^{-1} is assigned to the epoxide group, and adsorbance at about 800 cm^{-1} is assigned to the aromatic moieties. This aromatic band is taken as the internal thickness band. Adsorbance at about 1700 cm^{-1} is assigned to the carbonyl groups, but is was not used as an internal thickness band because it was found to be a function of extent of cure.

Figure 3. Thermograms obtained from Resin B using the Differential Scanning Calorimeter. The epoxy resin had initially been incompletely cured at 120°C for 4 hours. Calorimeter scan rate was 10°C per minute. The first run thermogram reveals a strong exothermic effect indicating additional curing reactions occurring during the experiment. The second run thermogram lacks such an exotherm and instead reveals a small baseline shift in the temperature range 495°K, suggestive of the glass-rubber transition. It is not clear whether the up-sweep of the baseline at the highest temperatures of these calorimetry runs is evidence for additional chemical reactions occurring in the upper temperature ranges.

Figure 4. Isothermal calorimeter runs obtained from epoxy Resin E held at 160°C. The first run curve corresponds to the instrumental output when uncured resin is placed in the preheated instrument stage. Second run curve is a duplicate of the first run, using the specimen that had been employed in the first run. Assuming the second run curve could serve as a "baseline", taking into

account all of the instrumental transient which existed in the first run, then a difference between the first and second run is simply the exothermic effect which occurs during this isothermal calorimetry experiment.

Figure 5. Integrating the data in the difference curve of Figure 4, permits construction of this plot of extent of cure versus curing time. Extent of cure has been based on independent infrared absorption experiments from the same specimens used in the calorimetry experiments. These data are obtained from epoxy Resin A.

Figure 6. Thermally Stimulated Discharge Current (TSDC) thermogram of the epoxy resin system, DGEBA cured with DETA at room temperature. The broad and structured discharge maximum observed in the temperature range, 120°K-250°K, is taken as the β relaxation peak.

Figure 7. TSDC thermogram for the same resin as in Figure 6 obtained over the temperature range from room temperature to 180°C. Note the higher poling temperature used in this experiment as opposed to Figure 6.

Figure 8. Integrating the β discharge peaks yields the stored charge which is released over the temperature range of the β peak. It is seen in this figure to be a linear function of the electrical field used for polarizing the sample.

Figure 9. TSDC thermogram obtained from epoxy Resin A cured at 140°C for 1½ hours and 5 hours.

Figure 10. TSDC thermogram obtained from epoxy Resin A cured for a short interval at 140, 158, and 181°C. It is seen that an increase in the curing temperature leads to an increase in the 170-180°K portion of the β peak.

Figure 11. The temperature-dependence of activation energy for epoxy Resin A, as studied in Figure 10.

Figure 12. TSDC thermogram of epoxy Resin B cured at 181°C for 2 hours and 12 hours.

Figure 13. The temperature-dependence of activation energy through the β peak region for epoxy Resin B, as studied in Figure 12.

Figure 14. TSDC thermogram of epoxy Resin E cured for two different intervals of time at 181°C.

Figure 15. Temperature-dependence of activation energy through the β relaxation range for epoxy Resin E, as studied in Figure 14.

Figure 16. TSDC thermograms from the different epoxy resins all cured at the same condition, 181°C for 12 hours. It is seen that the 170-180°K region of the β peak is strongest in that resin system (Resin A) which most completely reacts to make a macromolecular network.

Figure 17. Temperature-dependence of activation energies through the β peak region for each of the epoxy resins of Figure 16.

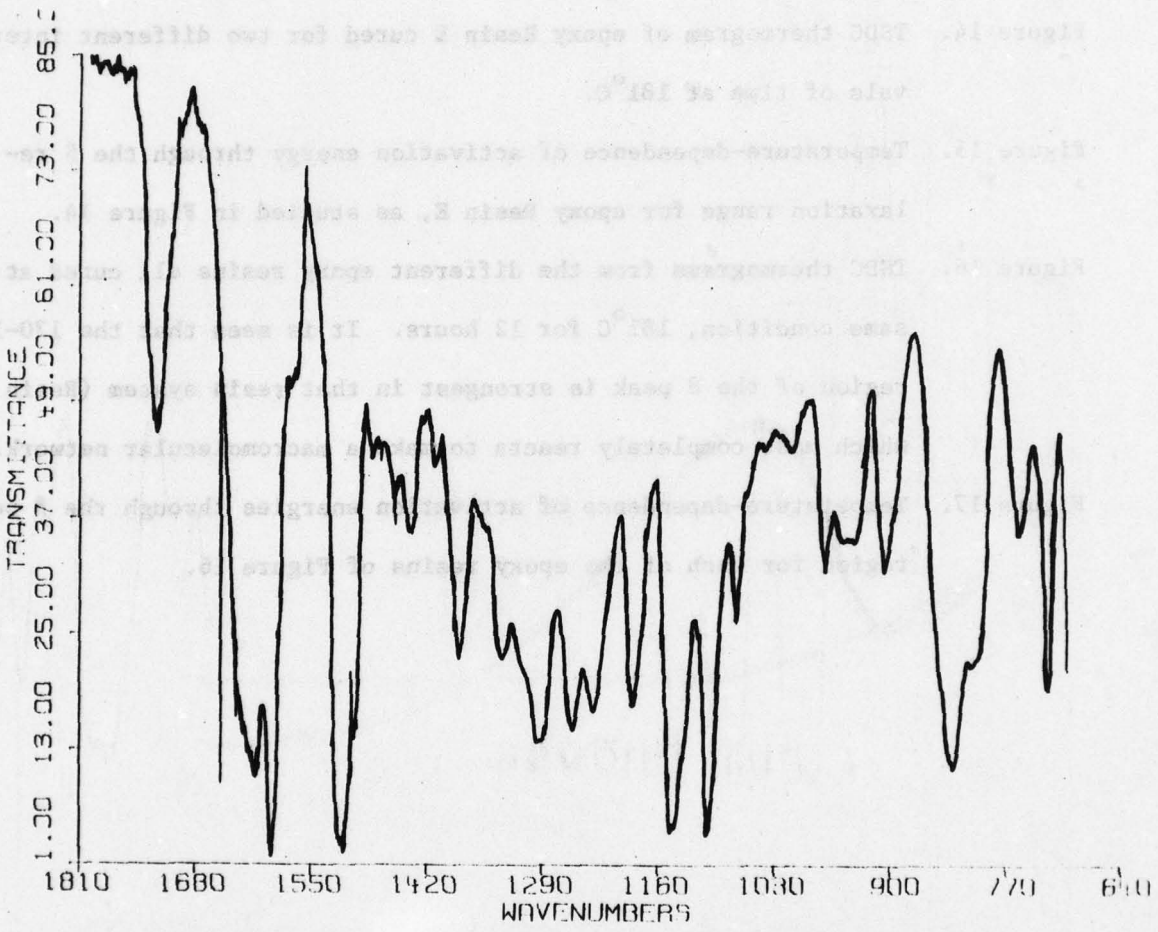
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FIGURE 1

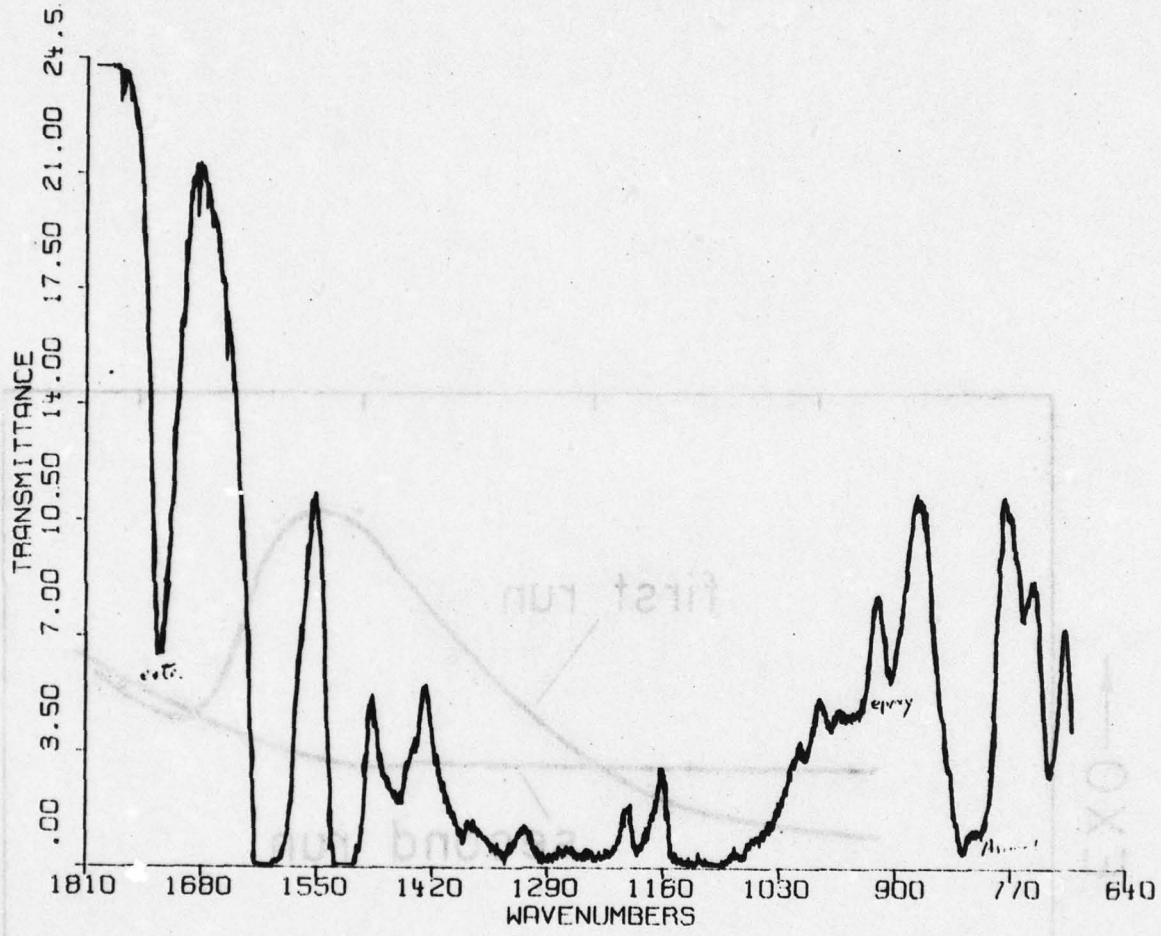
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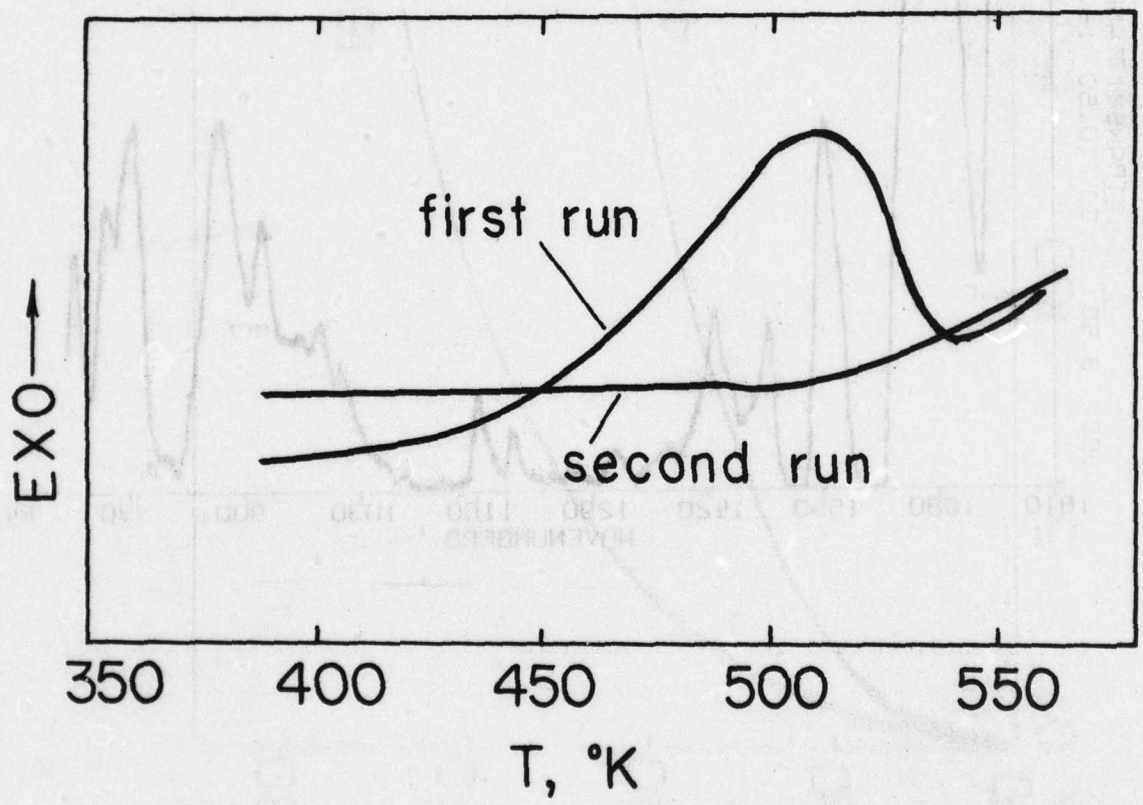
FIGURE 2

FIGURE 3



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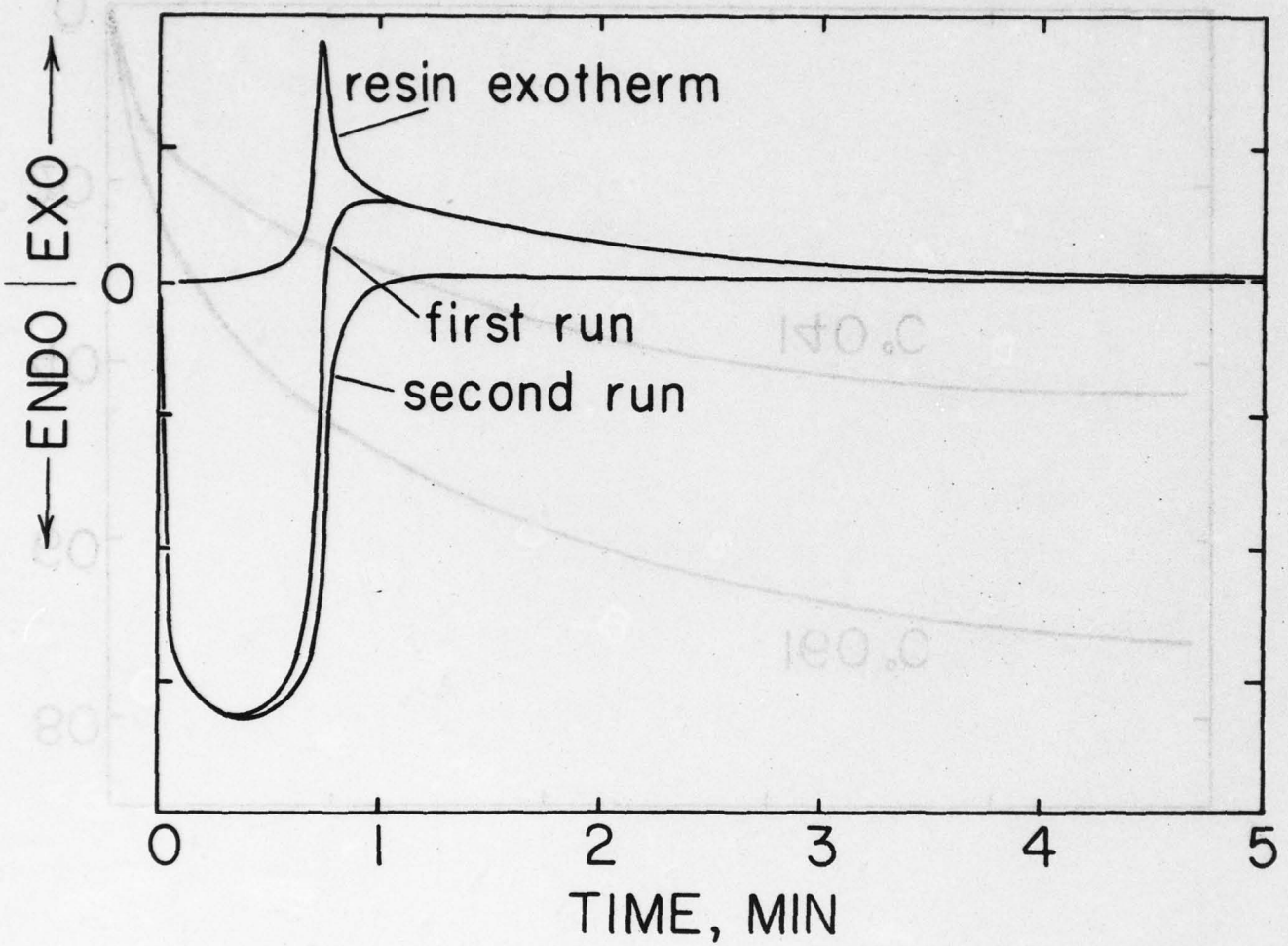
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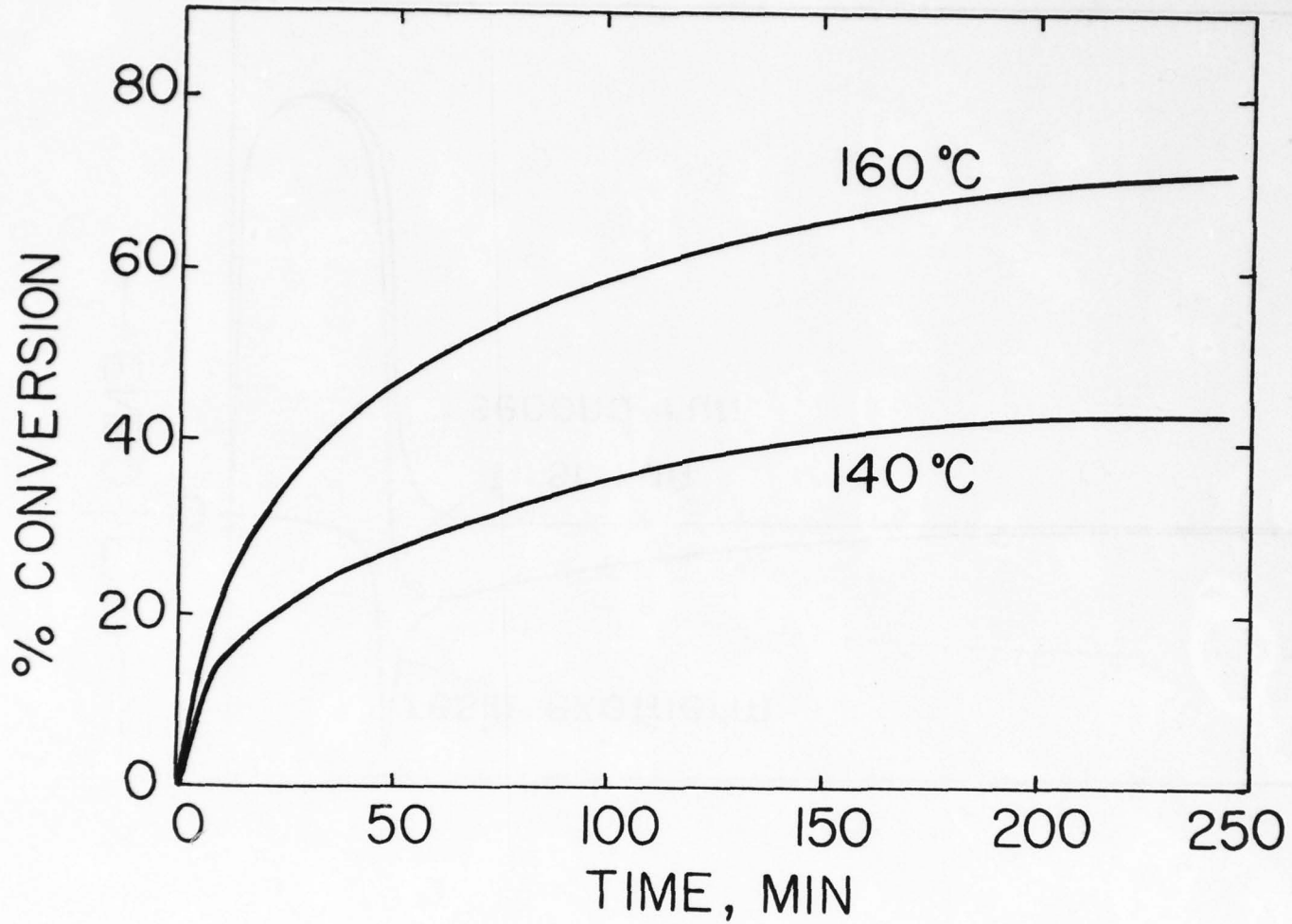
TIME, MIN

FIGURE 5



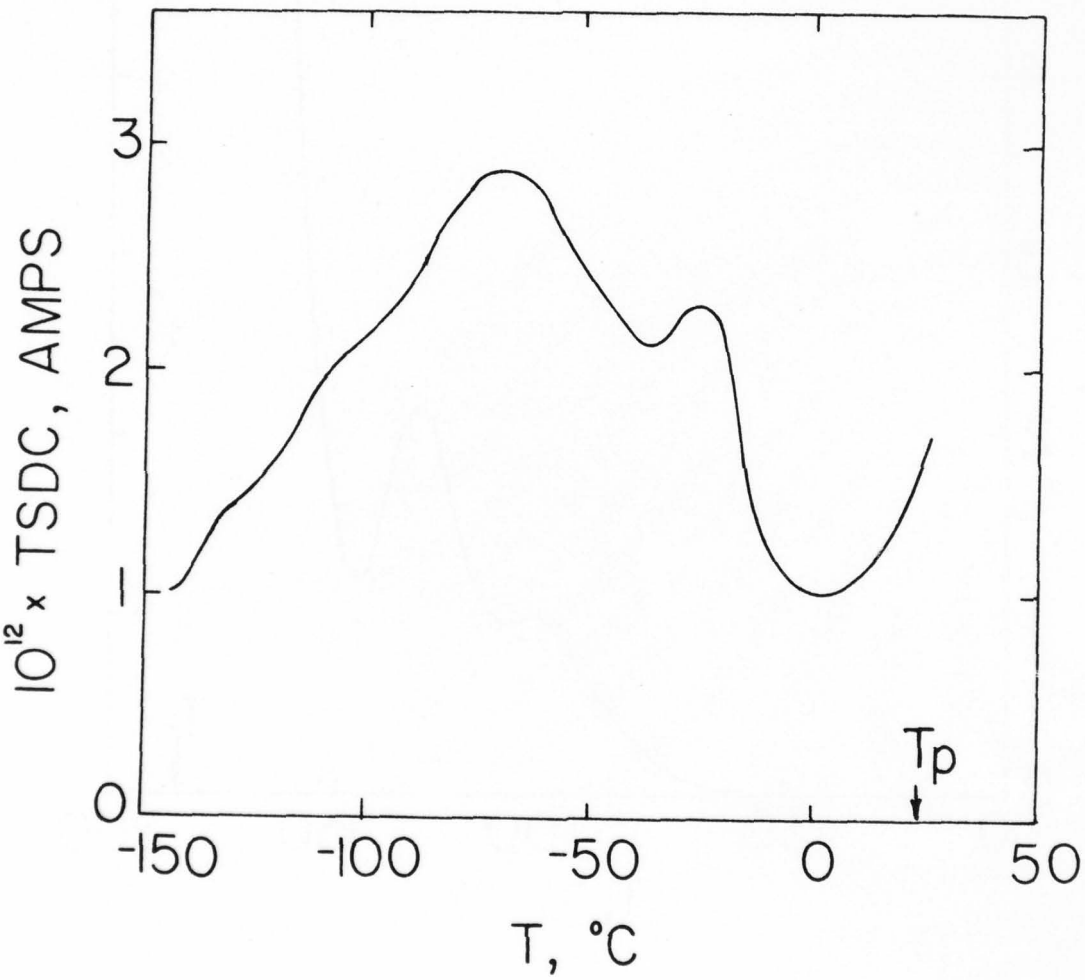


FIGURE 6

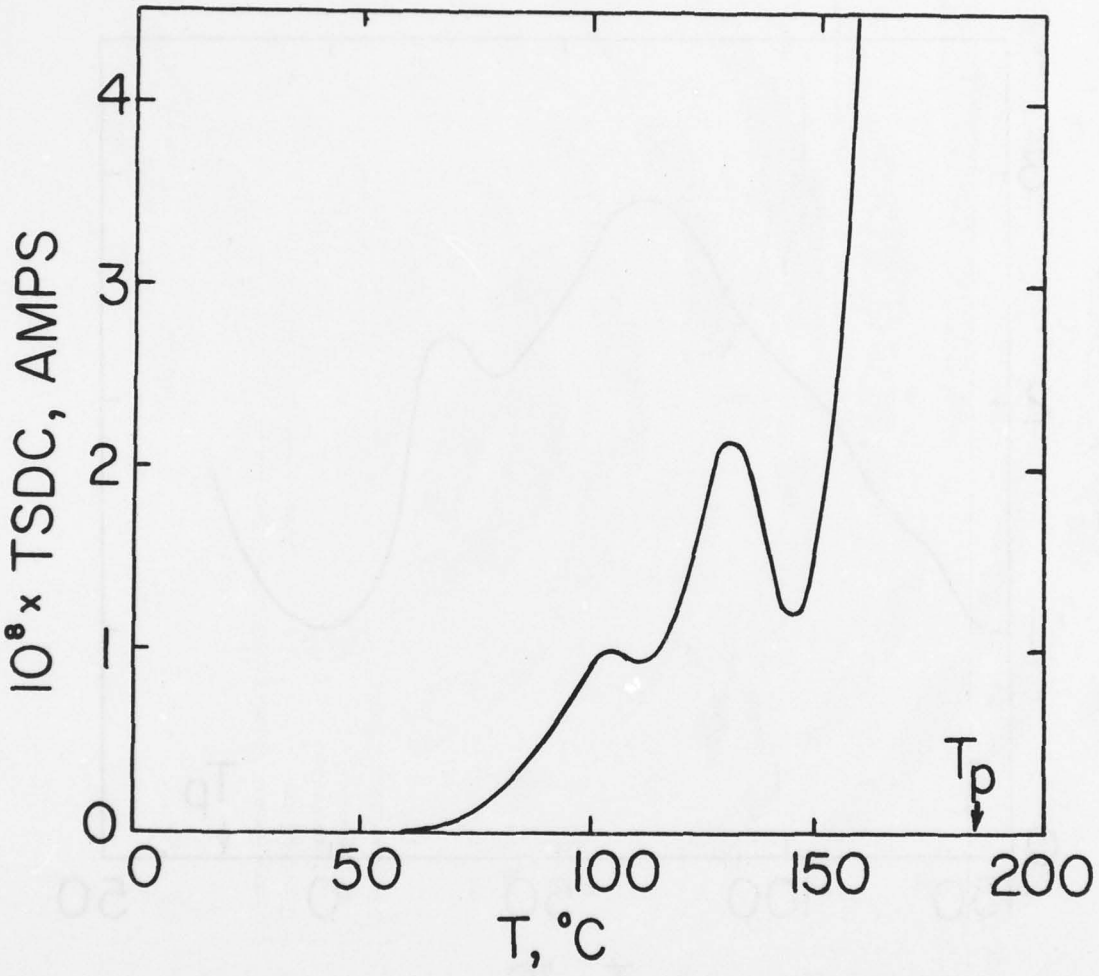


FIGURE 7

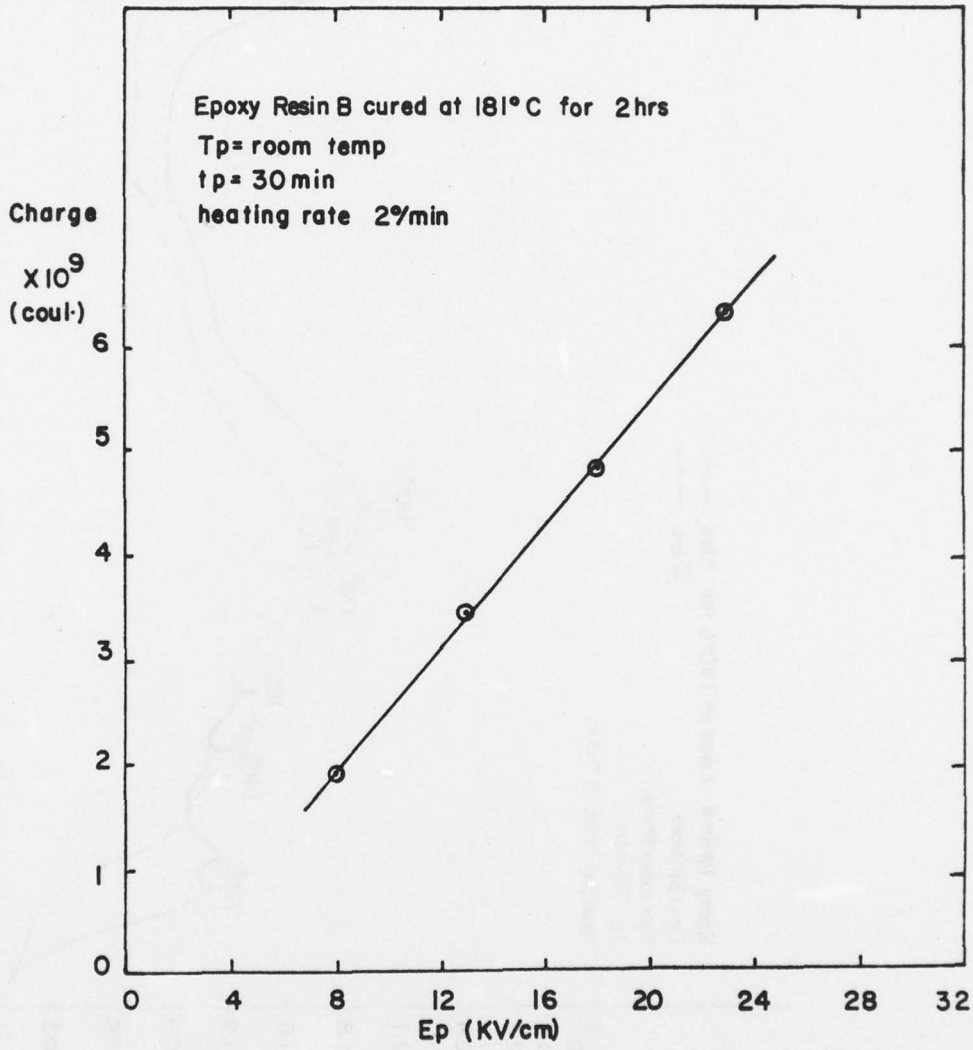

Epoxy Resin B cured at 181°C for 2hrs
Tp= room temp
tp= 30 min
heating rate 2°/min
Charge
X 10^9
(coul·)
0
1
2
3
4
5
6
0
4
8
12
16
20
24
28
32
Ep (KV/cm)

FIGURE 8

FIGURE 9

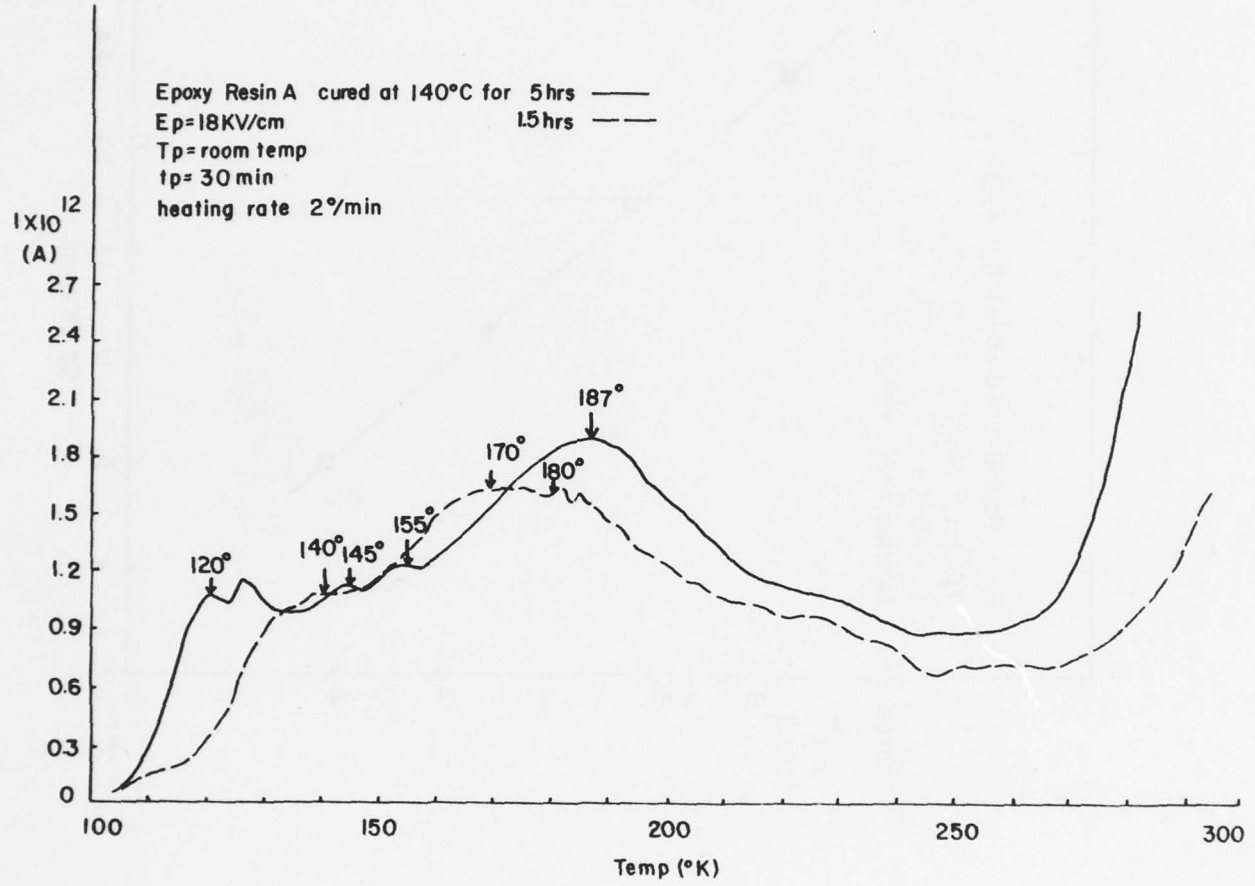
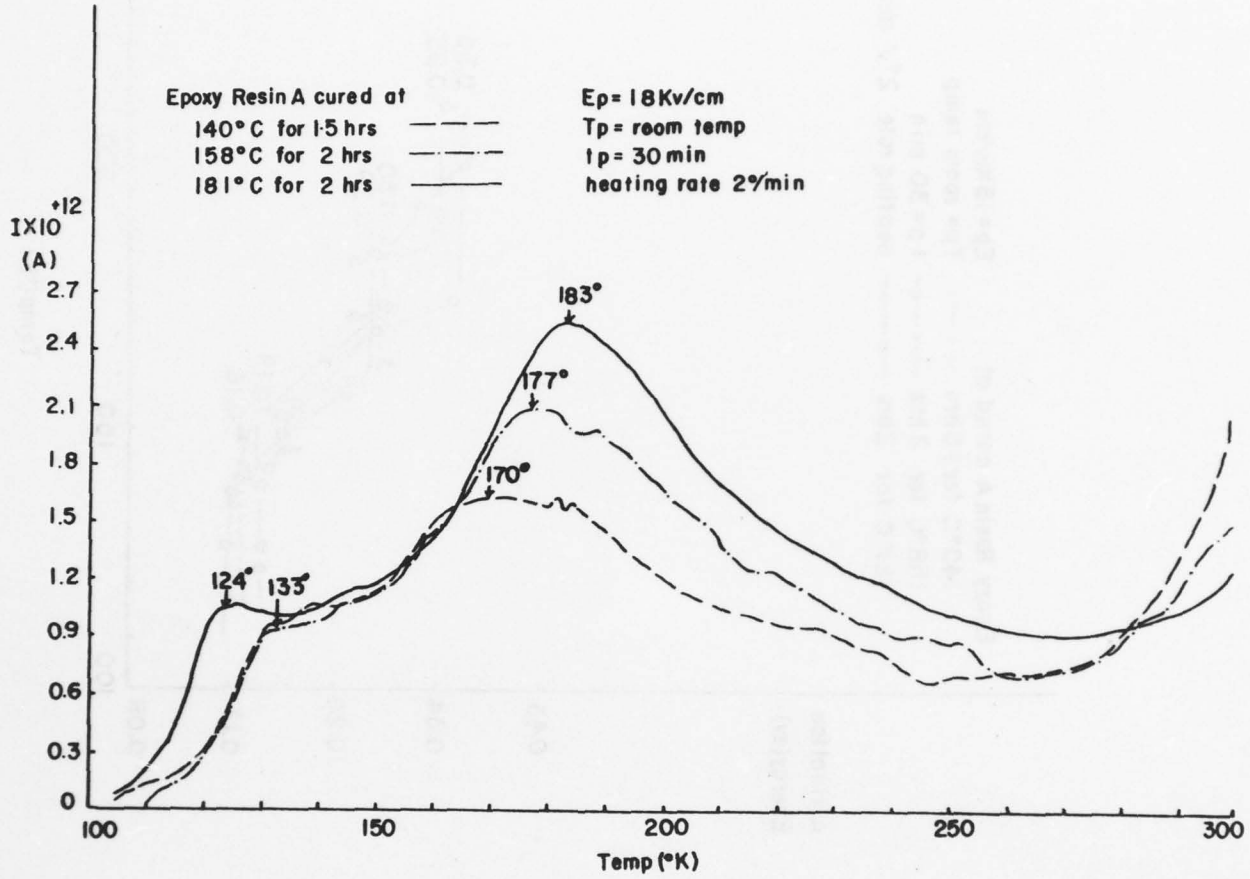

Epoxy Resin A cured at 140°C for 5 hrs
1.5 hrs
Ep = 18 KV/cm
Tp = room temp
tp = 30 min
heating rate 2°/min
1X10^12 (A)
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0
120°
140°
145°
155°
170°
180°
187°
100
150
200
250
300
Temp (°K)

FIGURE 10


Epoxy Resin A cured at
140° C for 1·5 hrs
158°C for 2 hrs
181°C for 2 hrs
Ep= 18Kv/cm
Tp= room temp
tp= 30 min
heating rate 2°/min
IX10+12
(A)
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0
183°
177°
170°
124°
133°
100
150
200
250
300
Temp (°K)

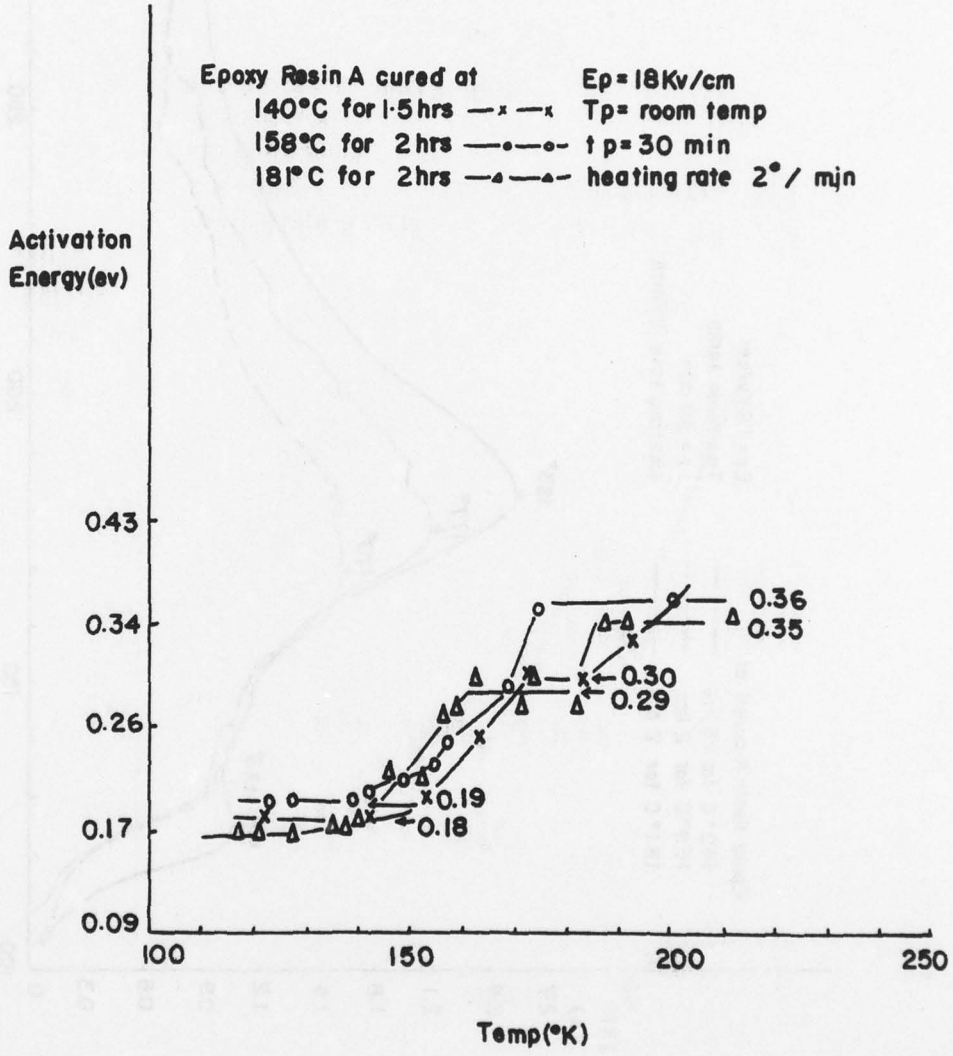
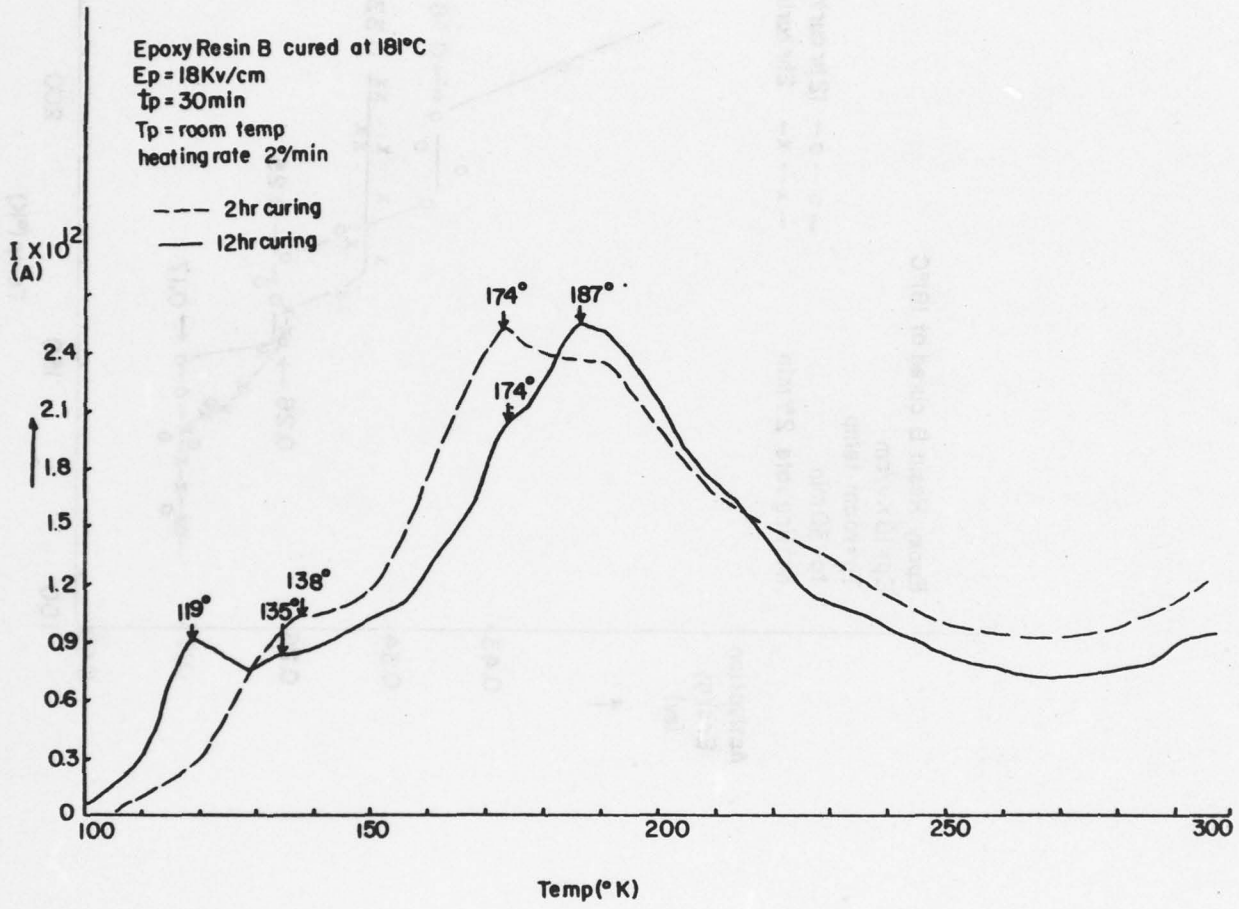

Epoxy Resin A cured at
140°C for 1·5 hrs —x—x
158°C for 2 hrs —o—o—
181°C for 2 hrs —Δ—Δ—
Ep = 18 Kv/cm
Tp = room temp
t p = 30 min
heating rate 2°/ min
Activation Energy(ev)
0.43
0.34
0.26
0.17
0.09
0.36
0.35
0.30
0.29
0.19
0.18
100
150
200
250
Temp(°K)

FIGURE 11

FIGURE 12


Epoxy Resin B cured at 181°C
Ep = 18Kv/cm
tp = 30min
Tp = room temp
heating rate 2°/min
2hr curing
12hr curing
I X 10^12 (A)
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0
174°
187°
174°
138°
135°
119°
100
150
200
250
300
Temp(° K)

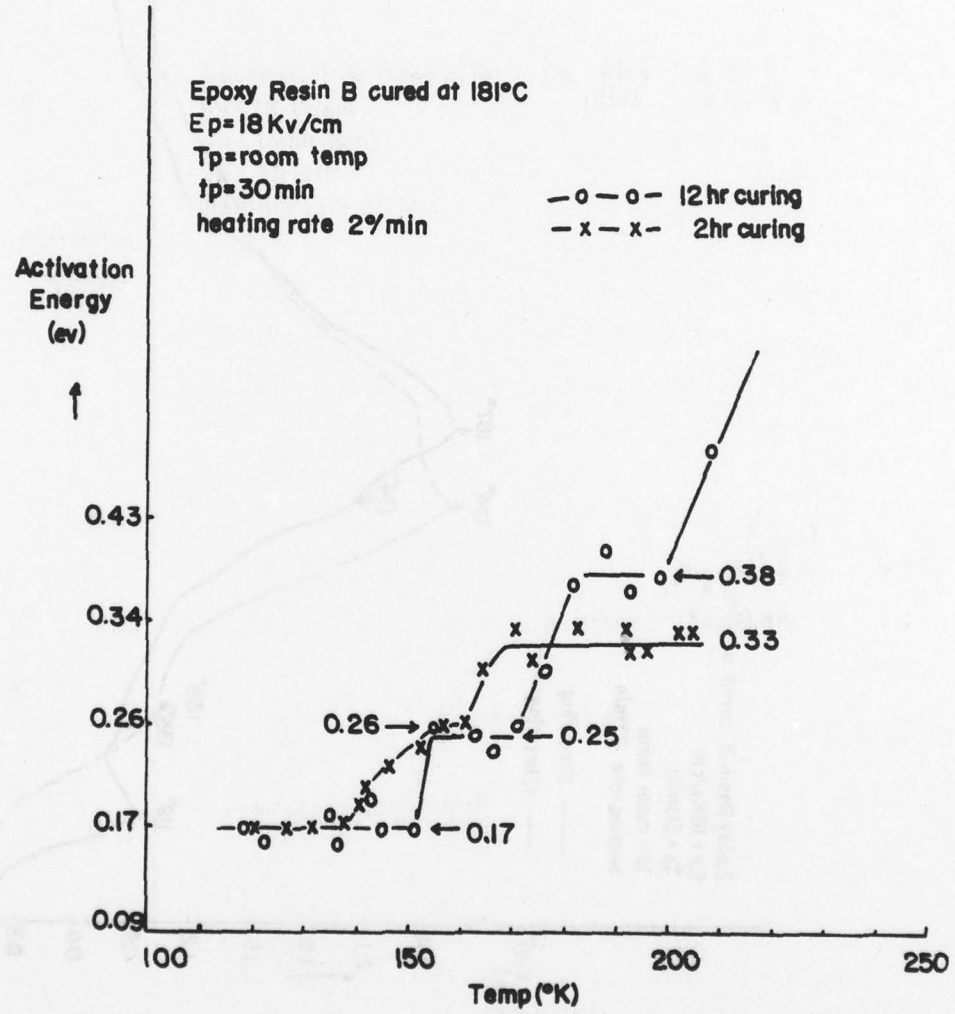
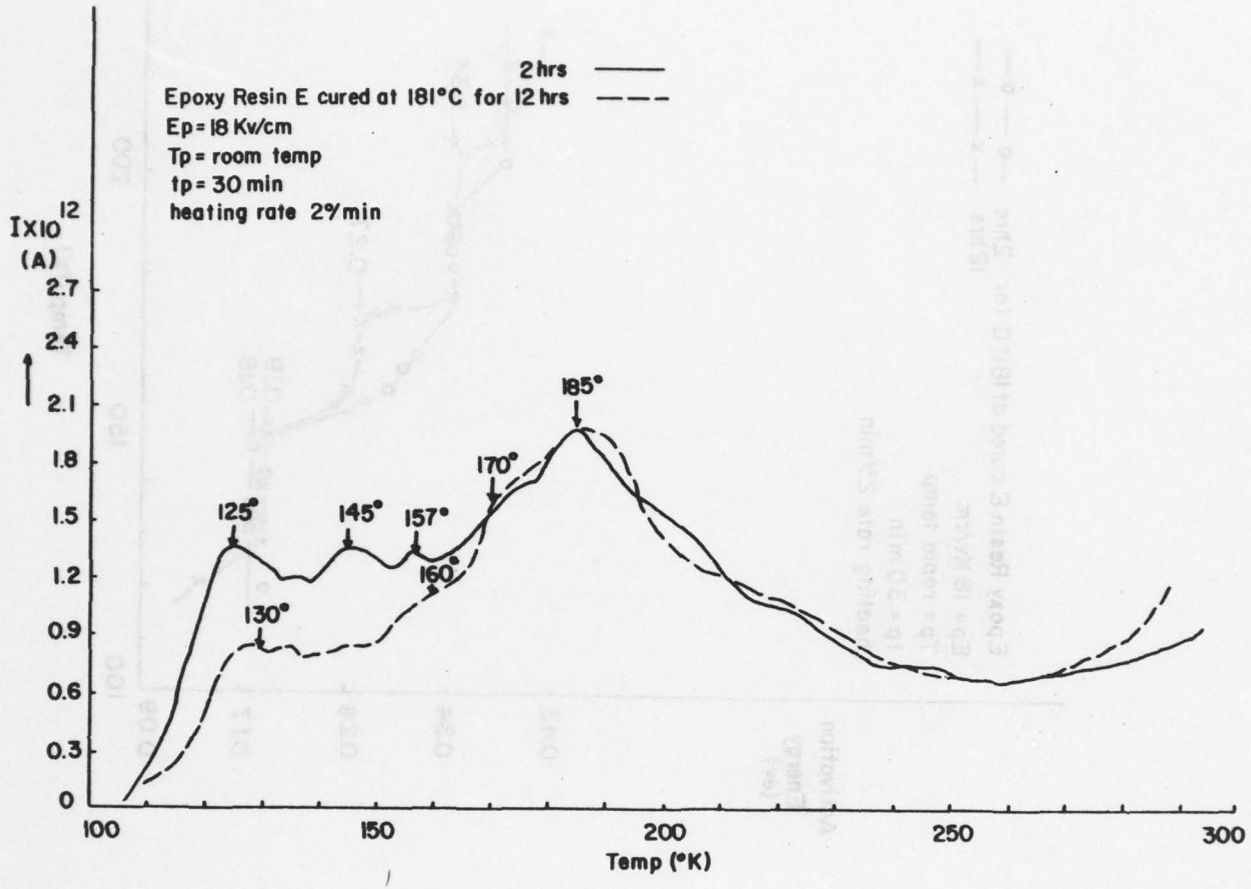

Epoxy Resin B cured at 181°C
Ep=18 Kv/cm
Tp=room temp
tp=30 min
heating rate 2°/min
—o—o— 12 hr curing
—x—x— 2hr curing
Activation Energy (ev)
0.43
0.34
0.26
0.17
0.09
0.38
0.33
0.26
0.25
0.17
100
150
200
250
Temp (°K)

FIGURE 13

FIGURE 14


2 hrs
Epoxy Resin E cured at 181°C for 12 hrs
Ep = 18 Kv/cm
Tp = room temp
tp = 30 min
heating rate 2°/min
I X 10^12 (A)
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0
125°
130°
145°
157°
160°
170°
185°
100
150
200
250
300
Temp (°K)

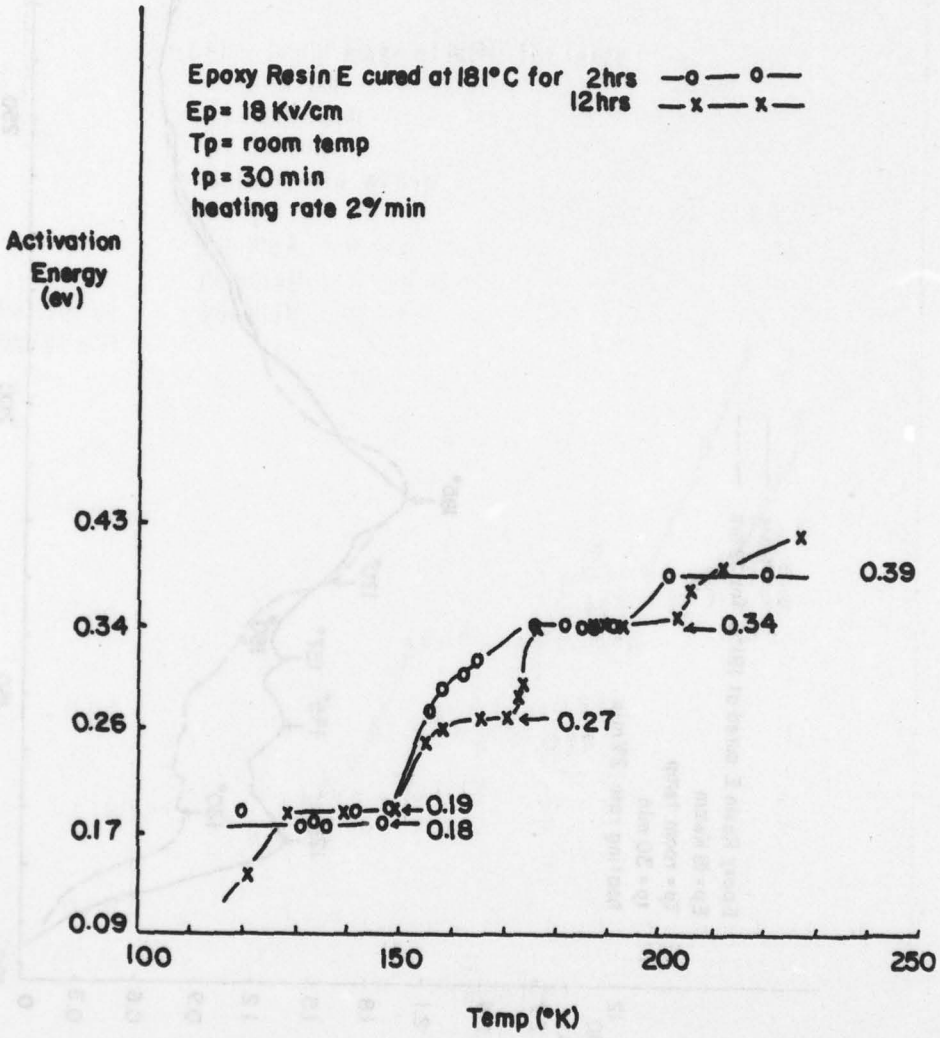
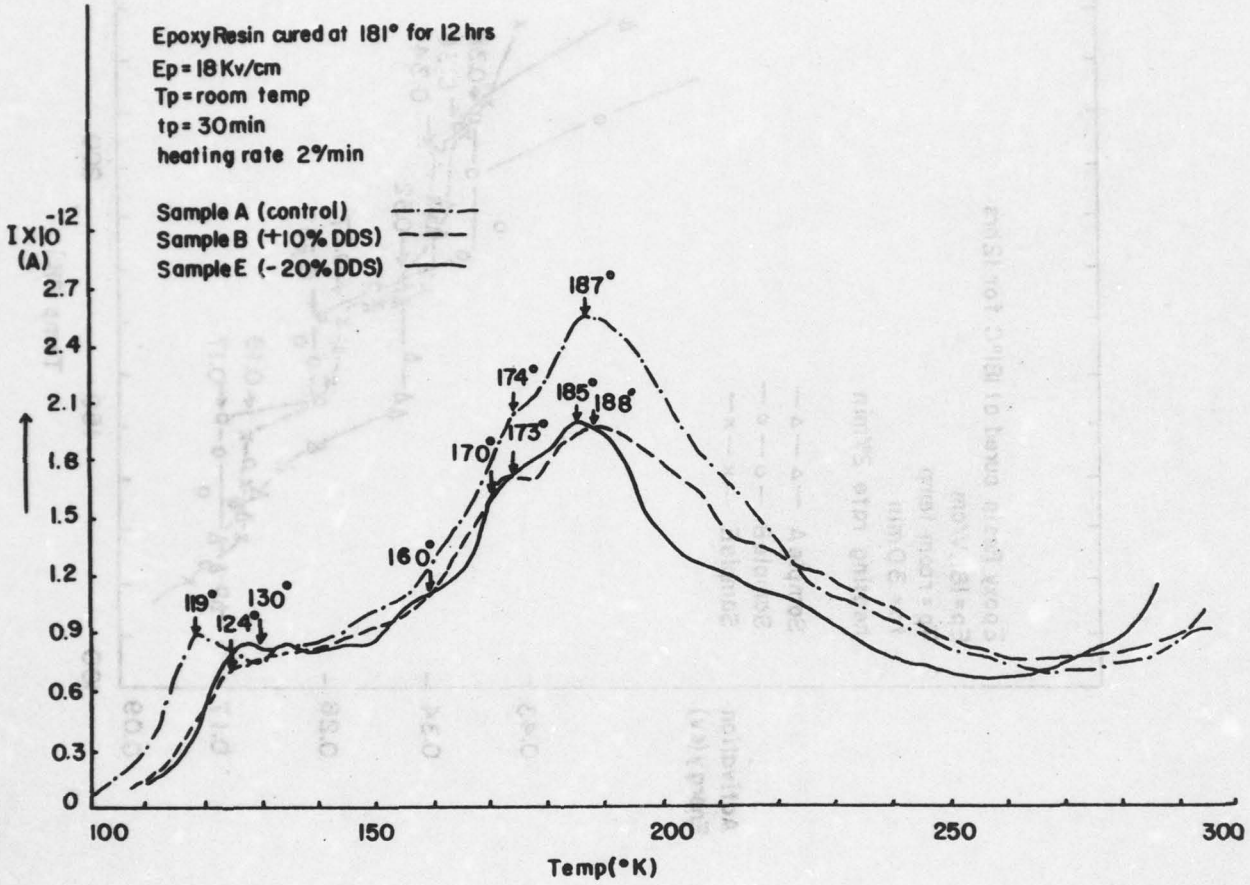

Epoxy Resin E cured at 181°C for 2hrs —o— o—
12hrs —x— x—
Ep= 18 Kv/cm
Tp= room temp
tp= 30 min
heating rate 2°/min
Activation Energy (ev)
0.43
0.34
0.26
0.17
0.09
0.39
0.34
0.27
0.19
0.18
100
150
200
250
Temp (°K)

FIGURE 15

FIGURE 16


Epoxy Resin cured at 181° for 12 hrs
Ep = 18 Kv/cm
Tp = room temp
tp = 30 min
heating rate 2°/min
Sample A (control)
Sample B (+10% DDS)
Sample E (-20% DDS)
I X 10^-12 (A)
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0
100
150
200
250
300
Temp(°K)
119°
124°
130°
160°
170°
174°
175°
185°
187°
188°

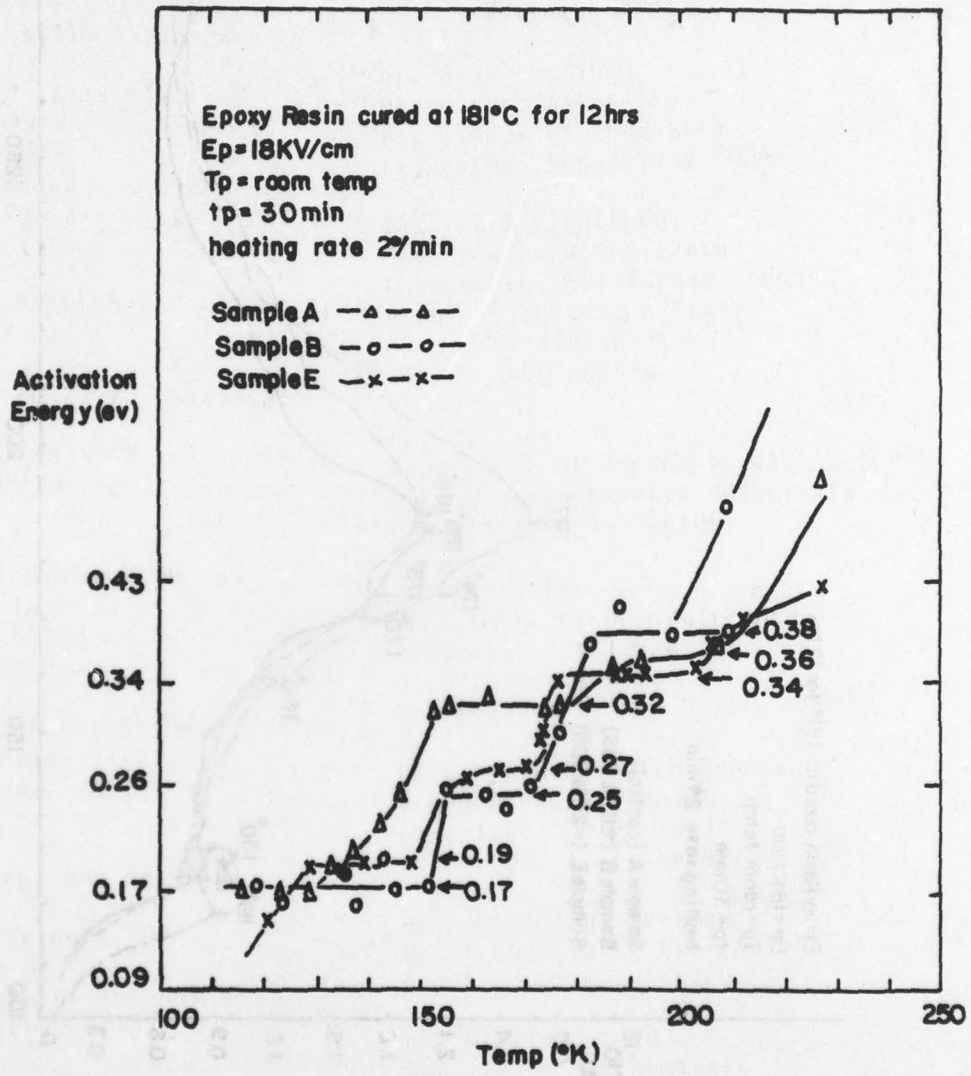

Epoxy Resin cured at 181°C for 12hrs
Ep=18KV/cm
Tp=room temp
tp=30min
heating rate 2°/min
Sample A —Δ—Δ—
Sample B —o—o—
Sample E —x—x—
Activation Energy (ev)
0.43
0.34
0.26
0.17
0.09
0.38
0.36
0.34
0.32
0.27
0.25
0.19
0.17
100
150
200
250
Temp (°K)

FIGURE 17

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